RN99119
Preliminary Amendment
PCT/FR00/02704

carrying a hydrogen atom on a triple bond, with an alkylation agent, in the presence of an anionisation agent.

24. (New) A process according to claim 23, wherein in that the starting mixed ether of benzyl/alkynyl type has the following general formula (I):

$$(R)_{n} \xrightarrow{\begin{array}{c} R_{1} \\ I \\ C \\ R_{2} \end{array}} C = C - H$$

wherein:

- A represents a residue of a cycle forming all or a part of an aromatic, monocyclic or polycyclic, carbocyclic or heterocyclic system comprising at least one group of formula:

(I)

- R represents one or more substituent(s), which are identical or different,
- R₁ and R₂, which are identical or different, represent a hydrogen atom, a functional group, a hydrocarbon group containing 1 to 24 carbon atoms, which is linear or branched, saturated or unsaturated, an acyclic, saturated or unsaturated, aliphatic group, a monocyclic, polycyclic or aromatic cycloaliphatic group, or a linear or branched, saturated or unsaturated aliphatic group having a cyclic substituent,
- R₃ and R₄, which are identical or different, represent a hydrogen atom or a hydrocarbon group containing 1 to 12 carbon atoms,

- n is a number smaller than or equal to equal to 5, and
- x is a number from 1 to 10.
- 25. (New) A process according to claim 24, wherein x is a number from 1 to 5.
- 26. (New) A process according to claim 23, wherein in that the starting mixed ether of benzyl/alkynyl type has the following general formula (I):

$$(R)_{n} \xrightarrow{R_{1}} C = C - H$$

$$R_{2} \xrightarrow{R_{1}} C \equiv C - H$$

wherein:

- A represents a residue of a cycle forming all or a part of an aromatic, monocyclic or polycyclic, carbocyclic or heterocyclic system comprising at least one group of formula:

(1)

- R represents one or more substituent(s), which are identical or different,
- R₁ and R₂, which are identical or different, represent:
 - a linear or branched, saturated or unsaturated, acyclic alkyl group, having an hydrocarbon chain, comprising 1 to 6 carbon atoms, the hydrocarbon chain being optionally interrupted by a heteroatom, or a functional group, and carrying optionally substituents,



- a linear or branched, saturated or unsaturated, acyclic aliphatic group carrying a cyclic substituent, being optionally substituted, said acyclic group being
- connected to the cycle via a covalent bond, a heteroatom or a functional group,
- a carbocyclic group, saturated or comprising 1 or 2 unsaturated bonds in the cycle, containing 3 to 8 carbon atoms in the cycle, said cycle being optionally substituted,
- an aromatic monocyclic carbocyclic group, containing at least 4 carbon atoms in the cycle, said cycle being optionally substituted, or
- a CF_3 group, for one of groups R_1 and R_2 .
- R₃ and R₄, which are identical or different, represent a hydrogen atom or a hydrocarbon group containing 1 to 12 carbon atoms,
- n is a number smaller than or equal to 5, and
- x is a number from 1 to 10.
- 27. (New) A process according to claim 24, wherein A is a residue of a cyclic compound comprising at least 4 carbon atoms in the cycle, optionally substituted, and representing at least one of the following cycles:
- an aromatic, monocyclic or polycyclic carbocycle, or
- an aromatic, monocyclic or polycyclic heterocycle comprising at least one heteroatom selected from the group consisting of O, N or S.
- 28. (New) A process according to claim 27, wherein A is a residue of a benzene or naphthalene cycle, optionally substituted.

- 29. (New) A process according to claim 27, wherein A carry one or more electron-donating group(s) selected from the group consisting of:
- linear or branched alkyl groups,
- linear or branched alkenyl groups,
- linear or branched halogenoalkyl groups,
- cycloalkyl groups comprising 3 to 6 carbon atoms,
- a phenyl group,
- alkoxy groups of formula R_5 -O- or thioether groups of formula R_5 -S-, wherein R_5 represents a linear or branched alkyl group comprising 1 to 6 carbon atoms, or a phenyl group,
- groups of formula $-N-(R_6)_2$, wherein R_6 groups, which are identical or different, represent a hydrogen atom, a linear or branched alkyl group comprising 1 to 6 carbon atoms, or a phenyl group, and
- a -CF₃ group.
- 30. (New) A process according to claim 27, wherein A carry one or more electron-donating group(s) selected from the group consisting of:
- linear or branched alkyl groups, comprising 1 to 4 carbon atoms,
- linear or branched alkenyl groups, comprising 2 to 4 carbon atoms,
- linear or branched halogenoalkyl groups, comprising 1 to 4 carbon atoms,
- a cyclohexyl group,
- a phenyl group,

M

- alkoxy groups of formula R_5 -O- or thioether groups of formula R_5 -S-, wherein R_5 represents a linear or branched alkyl group comprising 1 to 4 carbon atoms, or a phenyl group,
- groups of formula -N- $(R_6)_2$, wherein R_6 groups, which are identical or different, represent a hydrogen atom, a linear or branched alkyl group comprising 1 to 4 carbon atoms, or a phenyl group, and
- a -CF₃ group.
- 31. (New) A process according to claim 24, wherein n is greater than or equal to 2, two groups R and 2 successive atoms on the aromatic cycle being bonded together via an alkylene, alkenylene or alkenylidene group containing 2 to 4 carbon atoms, to form a saturated, unsaturated or aromatic heterocycle containing 5 to 7 carbon atoms, one or more carbon atoms being optionally replaced by a further heteroatom.
- 32. (New) A process according to claim 24, wherein n is greater than or equal to 2, two groups R and 2 successive atoms on the aromatic cycle being bonded together via an alkylene, alkenylene or alkenylidene group containing 2 to 4 carbon atoms, to form a saturated, unsaturated or aromatic heterocycle containing 5 to 7 carbon atoms, one or more carbon atoms being optionally replaced by a further oxygen atom.
- 33. (New) A process according to claim 24, wherein R_3 and R_4 , which are identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 12 carbon atoms.

- 34. (New) A process according to claim 33, wherein R₃ and R₄, which are identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.
- 35. (New) A process according to claim 23, wherein that the starting mixed ether of benzyl/alkynyl type has the following general formula (Ia):

$$(R)_{n} \leftarrow \begin{pmatrix} R_{1} \\ C \\ C \\ R_{2} \end{pmatrix} = \begin{pmatrix} R_{3} \\ C \\ C \\ R_{4} \\ X \end{pmatrix} \times C \equiv C - H$$

wherein:

- n is a number equal to or smaller than 4,

- x is a number equal to 1, 2 or 3,

- R group or groups are electron-donating groups,
- R₁ and R₂ groups, which are identical or different, represent:
 - a hydrogen atom,
 - a linear or branched alkyl group containing 1 to 6 carbon atoms,

(la)

- a cycloalkyl group containing 3 to 8 carbon atoms,
- a phenyl group,
- a phenylalkyl group containing 7 to 12 carbon atoms, or
- a CF₃ group, and
- R₃ and R₄ groups, which are identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.





36. (New) A process according to claim 23, wherein that the starting mixed ether of benzyl/alkynyl type has the following general formula (Ia):

$$(R)_{n} + C = C - H$$

wherein:

- n is 1 or 2,
- x is a number equal to 1, 2 or 3,
- R group or groups are methylenedioxy or ethylenedioxy groups,
- R_1 and R_2 groups, which are identical or different, represent:
 - a hydrogen atom,
 - a methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl group,

(la)

- a cyclopentyl or cyclohexyl group,
- a phenyl group,
- a benzyl group, or
- a CF₃ group, and
- R₃ and R₄ groups, which are identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.

AZ

RN99119
Preliminary Amendment
PCT/FR00/02704

37. (New) A process according to claim 23, wherein the starting mixed ether of benzyl/alkynyl type has the following formula (Ib):

$$(R)_{n} \leftarrow \begin{pmatrix} R_{1} \\ C \\ C \\ H \end{pmatrix} = \begin{pmatrix} R_{2} \\ C \\ C \\ R_{4} \\ X \end{pmatrix}_{X} = C - H$$
(Ib)

wherein:

- n is equal to 1 or 2,
- R group or groups represent an alkyl or alkoxy group containing 1 to 4 carbon atoms, or a methylenedioxy group, and
- R₁ represents a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.
- 38. (New) A process according to claim 23, wherein the starting mixed ether of benzyl/alkynyl type is [1-(prop-1-ynyloxy)ethyl]-3,4 dimethoxybenzene.
- 39. (New) A process according claim 23, wherein the alkylation agent is a dialkylsulphate or a halide compound.
- 40. (New) A process according to claim 39, wherein the alkylation agent is a dialkylsulphate having the following formula (IVa):

$$R_7$$
-O-SO₂-O-R₇ (IVa),

wherein R₇ represents a linear or branched alkyl group containing 1 to 6 carbon atoms.

41. (New) A process according to claim 39, wherein the alkylation agent is a halide compound having the following formula (IVb):

$$R_8$$
-X (IVb),

A2

RN99119
Preliminary Amendment
PCT/FR00/02704

wherein:

- R₈ represents a linear or branched, saturated or unsaturated, acyclic aliphatic hydrocarbon group containing 1 to 20 carbon atoms, a saturated, unsaturated or aromatic, monocyclic or polycyclic, cycloaliphatic group, or a linear or branched,

saturated or unsaturated aliphatic group carrying a cyclic substituent, and

- X represents a bromine, chlorine or iodine atom.

42. (New) A process according to claim 41, wherein X represents a chlorine atom or

an iodine atom and R₈ represents a linear or branched alkyl group containing 1 to 4

carbon atoms.

43. (New) A process according to claim 39, wherein the alkylation agent is

dimethylsulphate, methyl iodide, methyl chloride, chloroethane, methyl bromide or

bromoethane.

44. (New) A process according to claim 23, wherein the anionisation agent is an amide

base, a metallic alcoholate or an alkali metal.

45. (New) A process according to claim 44, wherein the anionisation agent is selected

from the group consisting of lithium diisopropylamide, lithium hexamethyldisilazane,

prepared or used in situ by the action of a strong lithiated base on a corresponding

amine, alkali metal alcoholates, sodium, and potassium.

46. (New) A process according to claim 45, wherein the alkali metal alcoholate is

sodium or potassium methylate, ethylate or tert-butylate.

47. (New) A process according to claim 45, wherein the anionisation agent is sodium

or potassium amide.



- 48. (New) A process according to claim 23, wherein the reaction is carried out in an organic solvent that is inert towards the anionisation agent.
- 49. (New) A process according to claim 48, wherein the organic solvent is an aliphatic or aromatic hydrocarbon.
- 50. (New) A process according to claim 23, wherein the temperature of the reaction is comprised between 20°C and a reflux temperature of the reaction mixture.
- 51. (New) A process according to claim 50, wherein the temperature is comprised between 50°C and 80°C.
- 52. (New) A process according claim 24, wherein the starting mixed ether of benzyl/alkynyl type of formula (I) and the anionisation agent are brought into contact in a reaction medium, the reaction medium being heated to a desired temperature, the alkylation agent being then added, and the substituted mixed ether of benzyl/alkynyl type obtained being recovered.